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The attached documents are exact copies of the European patent application described on the following page, as originally filed.

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Patentanmeldung Nr. Patent application No. Demande de brevet n°

98402934.8

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Blatt 2 der Bescheinigung
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- 1 -

TS 5549 EPC

CATALYTIC DEWAXING PROCESS

BACKGROUND OF THE INVENTION

The invention is related to a process for the catalytic dewaxing of a hydrocarbon oil feed including waxy molecules and more than 500 ppmw of sulphur or sulphur containing compounds with a catalyst composition comprising at least a binder, aluminosilicate zeolite crystallites and a Group VIII metal. The invention is especially directed to a process to prepare a lubricating base oil.

It is well known that catalysts comprising aluminosilicate zeolite crystallites will deactivate when used in a process for the catalytic dewaxing of a hydrocarbon oil feed in the presence of high amounts of sulphur. For example in US-A-5723716 it is stated that waxy feeds secured from natural petroleum sources will contain quantities of sulphur and nitrogen compounds which are known to deactivate wax hydroisomerisation catalysts. Exemplary catalysts described in this patent publication comprised palladium on zeolites having the TON topology. According to this patent specification this deactivation is prevented by using a feed containing no more than 10 ppm sulphur and no more than 2 ppm nitrogen.

WO-A-9801515 describes the dewaxing of an oil feed having a sulphur content of 45 ppmw and a nitrogen content of 1 ppmw using a dewaxing catalyst comprising 0.8 %w platinum supported on a carrier consisting of surface dealuminated ZSM-5 having a silica to alumina molar ratio of 51.6 and a silica binder (70 %w surface dealuminated ZSM-5 and 30 %w silica binder). According to this patent publication these low levels of sulphur and nitrogen in the dewaxing feedstock are needed because

10 sulphur and nitrogen are known to poison the noble metal-based dewaxing catalyst. According to this patent publication the sulphur and nitrogen contents are decreased in the oil feed by first hydrocracking the feed and subsequently separating a sulphur and nitrogen rich gaseous fraction from the liquid hydrocracker effluent.

15 US-A-4797266 describes in their examples a catalytic dewaxing process of a hydrocarbon oil feed containing 29 ppmw of nitrogen compounds and 2800 ppmw of sulphur compounds by using a combined ZSM-5/ferrierite/palladium containing catalyst. In order to maintain a constant pour point reduction the reaction temperature had to be raised by 1.9 °F per day due to catalyst activity decline. According to this publication the temperature raise in 20 case a ZSM-5/palladium catalyst was used was 6.3 °F per day.

25 WO-A-9641849 describes a dewaxing catalyst composition comprising palladium and/or platinum, an aluminosilicate zeolite crystallites having pores with a diameter in the range of from 0.35 to 0.80 nm and a low acidity refractory oxide binder material which is essentially free of alumina, wherein the surface of the aluminosilicate zeolite crystallites has been modified by subjecting the aluminosilicate zeolite crystallites to a 30 surface dealumination treatment. No indication is given in this publication that such a catalyst would be stable when using a feed with a high content of sulphur and nitrogen.

35 The object of this invention is a dewaxing process in which the decline in catalyst activity is less severe as in the process of US-A-4797266 when a hydrocarbon oil feed is used containing higher levels of sulphur compounds.

- 3 -

SUMMARY OF THE INVENTION

This object is achieved with the following process. Process for the catalytic dewaxing of a hydrocarbon oil feed including waxy molecules and more than 500 ppmw of sulphur or sulphur containing compounds by contacting the oil feed under catalytic dewaxing conditions with a catalyst composition comprising at least a hydrogenation component, dealuminated aluminosilicate zeolite crystallites and a low acidity refractory oxide binder material which is essentially free of alumina.

It has been found that the catalyst of the process according to the invention is very stable over time even though sulphur is present in the oil feed in a high content. This makes the process especially advantageous to replace solvent dewaxing process steps in an existing process to prepare lubricating base oils. In such a process the oil feed is suitably obtained by first distilling a crude petroleum feedstock at atmospheric pressures and subsequently performing a vacuum distillation on the residue of the atmospheric distillation. The distillate products obtained in the vacuum distillation, also referred to as vacuum distillates, are possible feedstocks from which the various lubricating base oils products are prepared. The boiling range of the vacuum distillates are suitably between 300 and 620 °C and preferably between 350 and 580 °C. Another feedstock for lubricating base oils are the residues of the above mentioned vacuum distillation which have been subjected to a deasphalting treatment.

Suitably undesirable aromatics will first be removed from the vacuum distillates and deasphalting vacuum residues by solvent extraction. Examples of possible solvents are phenol, furfural or N-methylpyrrolidone of which furfural is especially preferred. The mixture obtained in the solvent extraction is often referred to

as solvent extracted waxy raffinates. The solvent extraction step is suitably followed by a solvent dewaxing step in order to improve the pour point and the cloud point of the lubricating base oil product. The 5 solvents used in the solvent dewaxing step are for example methylethylketone (MEK) or liquid propane.

Because solvent dewaxing is a semi continuous process it is for operational reasons preferred to perform the dewaxing step by means of a catalytic dewaxing process 10 which can be performed continuously. Because known catalytic dewaxing processes are sensible to sulphur in the feedstock to be dewaxed, the oil feed is suitably first subjected to a hydrodesulphurization and/or a hydrodenitrogenation process step. Examples of these 15 hydrotreating processes are described in WO-A-9801515 and EP-A-304251. Hydrotreating results in that the sulphur levels in the oil feed are reduced. WO-A-9801515 illustrates a hydrotreatment by contacting the oil feed 20 at a pressure of 14 MPa in the presence of hydrogen a phosphorus promoted NiMo on (fluorided) alumina catalyst or a phosphorus promoted CoMo on (fluorided) alumina catalyst.

The present invention is also directed to replacing old and laborious solvent dewaxing processes with a 25 catalytic dewaxing process according to the invention without the need for hydrotreating at elevated pressure to reduce sulphur and the nitrogen content of the feed to the catalytic dewaxing hydroprocess.

DETAILED DESCRIPTION OF THE INVENTION

30 By catalytic dewaxing is here meant a process for decreasing the pour point of lubricating base oil products by selectively converting the components of the oil feed which impart a high pour point to products which do not impart a high pour point. Products which impart a 35 high pour point are compounds having a high melting

- 5 -

point. These compounds are referred to as waxes. Wax compounds include for example high temperature melting normal paraffins, iso-paraffins and mono-ringed compounds. The pour point is preferably reduced by at least 10 °C and more preferably by at least 20 °C.

Feedstock which may contain high amounts of sulphur and nitrogen are for example shale oils and gas oils. The invention is especially directed to a catalytic dewaxing process which is directed to the preparation of lubricating base oils. Examples of suitable feedstocks when the process according the invention is used to prepare lubricating base oils are the above mentioned solvent extracted waxy raffinates. Hydrotreated vacuum distillates or hydrotreated deasphalting vacuum residues will normally contain less than 500 ppmw of sulphur. If however the hydrocarbon oil, obtained by hydrotreating a vacuum distillate or a deasphalting vacuum residue, contains higher sulphur contents it may be advantageously used in the process according to the invention.

The process according to the invention is related to a dewaxing process in which the amount of sulphur in the oil feed is more than 500 ppmw and especially more than 750 ppmw and more especially higher than 1000 ppmw. The upper limit of the sulphur in the oil feed is suitably 15000 ppmw. It has been found that the oil feed may additionally contain nitrogen. Nitrogen compounds are also known to influence the stability of a dewaxing catalyst in a negative manner. For example in US-A-5273645 it is disclosed that not all solvent extracted raffinates can be subsequently catalytically dewaxed. The high-nitrogen content levels, particularly basic nitrogen compounds, in certain solvent-extracted raffinates can cause a rapid deactivation of the dewaxing catalysts. With the process according to the invention has now been found that hydrocarbon mixtures containing

- 6 -

more than 10 ppmw of nitrogen compounds can be used as oil feed in the present process without experiencing a deactivation of the catalyst. The oil feed preferably contains less than 600 ppmw of nitrogen compounds and 5 more preferably less than 400 ppmw of nitrogen compounds. The content of sulphur and nitrogen compounds here mentioned is calculated as the weight fraction of atomic sulphur and/or nitrogen.

Catalytic dewaxing conditions are known in the art 10 and typically involve operating temperatures in the range of from 200 to 500 °C, preferably from 250 to 400 °C, hydrogen pressures in the range of from 10 to 200 bar, preferably from 15 to 100 bar, more preferably from 15 to 65 bar, weight hourly space velocities (WHSV) in the 15 range of from 0.1 to 10 kg of oil per litre of catalyst per hour (kg/l/hr), preferably from 0.2 to 5 kg/l/hr, more preferably from 0.5 to 3 kg/l/hr and hydrogen to oil ratios in the range of from 100 to 2,000 litres of 20 hydrogen per litre of oil.

25 The catalyst composition used in the present invention comprises a hydrogenation component, a surface dealuminated aluminosilicate zeolite crystallites and a low acidity refractory oxide binder material which is essentially free of alumina. Examples of such catalysts are described in WO-A-9641849.

30 The aluminosilicate zeolite crystallites preferably has pores with a diameter in the range of from 0.35 to 0.80 nm. This diameter refers to the maximum pore diameter. As is generally recognised, the pores in a molecular sieve are polygonal shaped channels having a minimum and a maximum pore diameter. For the purpose of the present invention the maximum pore diameter is the critical parameter, because it determines the size of the waxy molecules which can enter the pores. Examples of 35 aluminosilicate zeolites are aluminosilicates mordenite,

- 7 -

zeolite beta, ferrierite, ZSM-11, ZSM-12, ZSM-22, ZSM-23, ZSM-35, ZSM-38, ZSM-48, ZSM-57, SSZ-23, SSZ-24, SSZ-25, SSZ-26, SSZ-32, SSZ-33 and MCM-22 and mixtures of two or more of these. Preferred aluminosilicate zeolites are of the MFI-topology for example ZSM-5.

The crystallite size of the zeolite may be as high as 100 micron. Preferably small crystallites are used in order to achieve an optimum catalytic activity.

Preferably crystallites smaller than 10 micron and more preferably smaller than 1 micron are used. The practical lower limit is suitably 0.1 micron.

The dewaxing catalyst composition used in the present process also comprises a low acidity refractory oxide binder material which is essentially free of alumina.

Examples are low acidity refractory oxides such as silica, zirconia, titanium dioxide, germanium dioxide, boria and mixtures of two or more of these. The most preferred binder is silica. The weight ratio of modified molecular sieve to binder is suitably within the range of from 05/95 to 95/05.

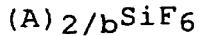
The dealumination of the aluminosilicate zeolite results in a reduction of the number of alumina moieties present in the zeolite and hence in a reduction of the mole percentage of alumina. The expression "alumina moiety" as used in this connection refers to an Al_2O_3 -unit which is part of the framework of the aluminosilicate zeolite, i.e. which has been incorporated via covalent bindings with other oxide moieties, such as silica (SiO_2), in the framework of the aluminosilicate zeolite. The mole percentage of alumina present in the aluminosilicate zeolite is defined as the percentage of moles Al_2O_3 relative to the total number of moles of oxides constituting the aluminosilicate zeolite (prior to dealumination) or modified molecular sieve (after dealumination).

- 8 -

Preferably the surface of the zeolite crystallites are selectively dealuminated. A selective surface dealumination results in a reduction of the number of surface acid sites of the zeolite crystallites, whilst not affecting the internal structure of the zeolite crystallites.

Dealumination can be attained by methods known in the art. Particularly useful methods are those, wherein the dealumination selectively occurs, or anyhow is claimed to occur selectively, at the surface of the crystallites of the molecular sieve. Examples of dealumination processes are described in the afore mentioned WO-A-9641849.

Preferably dealumination is performed by a process in which the zeolite is contacted with an aqueous solution of a fluorosilicate salt wherein the fluorosilicate salt is represented by the formula:



wherein 'A' is a metallic or non-metallic cation other than H⁺ having the valence 'b'. Examples of cations 'b' are alkylammonium, NH₄⁺, Mg⁺⁺, Li⁺, Na⁺, K⁺, Ba⁺⁺, Cd⁺⁺, Cu⁺, Ca⁺⁺, Cs⁺, Fe⁺⁺, Co⁺⁺, Pb⁺⁺, Mn⁺⁺, Rb⁺, Ag⁺, Sr⁺⁺, Tl⁺, and Zn⁺⁺. Preferably 'A' is the ammonium cation. The zeolite material may be contacted with the fluorosilicate salt at a pH of suitably between 3 and 7. Such a dealumination process is for example described in US-A-5157191. The dealumination treatment is referred to as the AHS-treatment.

The catalyst composition is preferably prepared by first extruding the aluminosilicate zeolite with the binder and subsequently subjecting the extrudate to a dealumination treatment, preferably the AHS treatment as described above. It has been found that an increased mechanical strength of the catalyst extrudate is obtained when prepared according to this sequence of steps.

- 9 -

The hydrogenation component suitably comprises at least one Group VIB metal component and/or at least one Group VIII metal component. Group VIB metal components include tungsten, molybdenum and/or chromium as sulphide, oxide and/or in elemental form. If present, a Group VIB metal component is suitably present in an amount of from 1 to 35% by weight, more suitably from 5 to 30% by weight, calculated as element and based on total weight of support, i.e. modified molecular sieve plus binder.

5 Group VIII metal components include those components based on both noble and non-noble metals. Particularly suitable Group VIII metal components, accordingly, are palladium, platinum, nickel and/or cobalt in sulphidic, oxidic and/or elemental form. Nickel and/or cobalt, if present at all, may be present in an amount in the range of from 1 to 25% by weight, preferably 2 to 15% by weight, calculated as element and based on total weight of support. The total amount platinum or palladium will suitably not exceed 10% by weight calculated as element and based on total weight of support, and preferably is in the range of from 0.1 to 5.0% by weight, more preferably from 0.2 to 3.0% by weight. If both platinum and palladium are present, the weight ratio of platinum to palladium may vary within wide limits, but suitably is in the range of from 0.05 to 10, more suitably 0.1 to 5.

10 Catalysts comprising palladium and/or platinum as the hydrogenation component are preferred. Most preferred is when platinum is used as the sole hydrogenation component. The hydrogenation component is suitably added to the catalyst extrudate comprising the dealuminated aluminosilicate zeolite crystallites by known techniques.

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The invention will be illustrated by the following non-limiting examples.

- 10 -

EXAMPLE 1

A dealuminated ZSM-5 catalyst was prepared according to the following procedure. ZSM-5 (obtained from PQ company) was extruded with a silica binder (70% by weight of ZSM-5 with a silica-alumina ratio of 50 and 30% by weight of silica binder). The extrudates were dried for 4 hours at 120 °C and then calcined for 2 hours at 550 °C. 1329 ml of a 0.11 N ammonium hexafluorosilicate solution were added to a slurry containing 60 grams of the thus obtained extrudate and 590 ml deionised water. The reaction mixture was heated to 100 °C and with gentle stirring maintained at this temperature for 17 hours. After filtration, the extrudates were washed with deionised water and dried at 120 °C for 2 hours and calcined for 2 hours at 480 °C.

Subsequently said modified silica-bound ZSM-5 was ion-exchanged with an aqueous solution of platinum tetramine hydroxide followed by drying (2 hours at 120 °C) and calcining (2 hours at 300 °C). The catalyst was activated by reduction of the platinum under a hydrogen rate of 100 l/hr at a temperature of 350 °C for 2 hours resulting in a catalyst containing 0.7 wt% platinum.

Subsequently a waxy raffinate having the properties as listed in Table I was contacted in the presence of hydrogen with the above prepared catalyst at a temperature of 345 °C, an outlet pressure of 40 bar, a weight hourly space velocity (WHSV) of 1.0 kg/l.hr and a once through gas rate of 700 Nl/kg.

- 11 -

Table 1

Density (d _{70/4})	0.8407	Flash point	>250 °C
Refractive index (n _{70/D})	1.464	Pour point	+48 °C
Viscosity at 80 °C (mm ² /s)	16.63	IBP	384 °C
Viscosity at 100 °C (mm ² /s)	9.84	T50	501 °C
Viscosity at 120 °C (mm ² /s)	6.48	FBP	588 °C
Sulphur (mg/kg)	7100		
Nitrogen (mg/kg)	42		

pour point measured by NF T 60-105, Initial boiling point (IBP), T50 and final boiling point (FBP) measured by ASTM D 2892m, kinematic viscosities by NF-EN-ISO 3104, sulphur by ASTM D 5453, nitrogen content by SMS 2695m.

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The results of the experiment are summarised in Table 2.

- 12 -

Table 2

on stream time (hours)	0	95	175	295	970
temperature (°C)	345	345	345	345	345
gas make (w%)	16.7	17.8	17.1	17.7	17.4
390 °C ⁺ yield (w% on feed)	75.5	76.2	76.0	75.8	75.7
viscosity at 40 °C (cSt)	114.5	114.8	114.3	114.7	113.9
viscosity at 100 °C (cSt)	11.9	11.9	11.9	11.9	11.9
viscosity index (VI)	91	91	92	91.5	91.5
pour point (± 1 °C)	-11	-10	-10	-11	-8

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The results in Table 2 show that for almost 1000 hours of on-stream time a product of constant the same good quality can be obtained without having to increase the operating temperature. The need to increase the operating temperature in order to maintain a constant product quality when the dewaxing catalyst deactivates is for example described in the earlier mentioned US-A-4797266 and EP-A-304251.

- 13 -

TS 5549 EPCC L A I M S

1. Process for the catalytic dewaxing of a hydrocarbon oil feed including waxy molecules and more than 500 ppmw of sulphur or sulphur containing compounds by contacting the oil feed under catalytic dewaxing conditions with a catalyst composition comprising at least a hydrogenation component, dealuminated aluminosilicate zeolite crystallites and a low acidity refractory oxide binder material which is essentially free of alumina.
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2. Process according to claim 1, wherein the oil feed comprises more than 750 ppmw of sulphur or sulphur containing compounds.
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3. Process according to any one of claims 1-2, wherein the oil feed comprises more than 10 ppmw of nitrogen or nitrogen containing compounds.
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4. Process according to any one of claims 1-3, wherein the oil feed is a solvent extracted waxy raffinate.
5.
5. Process according to any one of claims 1-4, wherein the hydrogenation component is platinum.
6.
6. Process according to any one of claims 1-5, wherein the low acidity binder is silica.
20
7. Process according to any one of claims 1-6, wherein the aluminosilicate zeolite crystallites have pores with a diameter in the range of from 0.35 to 0.80 nm.
7.
8. Process according to claim 7, wherein the aluminosilicate zeolite crystallites is of the MFI type.
25
9. Process according to any one of claims 1-8, wherein the dealuminated aluminosilicate zeolite crystallites are obtained by contacting the zeolite crystallites with an aqueous solution of a fluorosilicate salt wherein the fluorosilicate salt is represented by the formula:
30

(A) $2/b \text{SiF}_6$

- 14 -

wherein 'A' is a metallic or non-metallic cation other than H^+ having the valence 'b', preferably ammonium.

10. Process according to any one of claims 9, wherein an
5 extrudate of the aluminosilicate zeolite crystallites and the low acidity binder is contacted with the aqueous solution of the fluorosilicate salt.

11. Method for retrofitting a process for preparing lubricating base oils wherein an existing solvent
10 dewaxing step is replaced by a catalytic dewaxing process according to any one of claims 1 to 10.

V25/TS5549PD

- 15 -

TS 5549 EPC

A B S T R A C T

CATALYTIC DEWAXING PROCESS

Process for the catalytic dewaxing of a hydrocarbon oil feed including waxy molecules and more than 500 ppmw of sulphur or sulphur containing compounds by contacting the oil feed under catalytic dewaxing conditions with a catalyst composition comprising at least a hydrogenation component, dealuminated aluminosilicate zeolite crystallites and a low acidity refractory oxide binder material which is essentially free of alumina.

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